Petroleum Coke: Composition, Aquatic Toxicity, and Fate

Issue

What are the potential impacts to human health (from a surface water exposure pathway) and aquatic life from petroleum coke piles located along the Detroit River?

Composition[1, 2]

There are two forms of petroleum coke, green coke and a more refined product, calcinated coke. The material of interest is green coke.

Green coke is primarily composed of elemental carbon, with up to 15% residual hydrocarbons (including polycyclic aromatic hydrocarbons (PAHs) (~25 mg/kg), sulfur (~2.5-5%), and heavy metals, primarily nickel (250-500 mg/kg) and vanadium (~1,000-2,000 mg/kg).

Environmental Fate

EPA characterizes petroleum coke as essentially inert[1]. Petroleum coke is highly persistent in the environment, with low rates of vapor pressure, water solubility, volatilization, hydrolysis, and photooxidation[1]. Bioaccumulation potential is low[1]. If released to the aquatic environment, petroleum coke will either be incorporated into sediment or float on the surface. The rate at which this occurs depends on particle size and density relative to water[2].

Mammalian Toxicity

Mammalian toxicity studies on green coke are based primarily on inhalation or dermal exposure, since this would be the primary route of exposure of humans to green coke[1,2]. No oral toxicity studies were found for green coke. However, human health values for surface waters protected as a drinking water source are available for the principal metals found in green coke, vanadium and nickel. The human health values for these two metals are 53 ug/L and 2,600 ug/l, respectively.

Aquatic Life Toxicity

Green Coke Toxicity to Aquatic Life[2]

Acute toxicity tests were performed on water-accommodated fractions (WAF) determined to obtain the highest extractability of material from green coke. WAF is the fraction of the material that can be leached into water by low-energy mixing. To prepare WAF, green coke pellets milled and sieved to about 2 mm size were added to water and mixed. The WAF was the water fraction after mixing, with solid green coke removed. Based on the way the WAF was prepared, EPA was satisfied that this approach adequately replicated the effects of slow, long-term leaching of materials from green coke on aquatic life.

Green coke WAF acute toxicity was very low. A 1,000 mg/L (0.1%) WAF concentration did not adversely affect fathead minnows following 96 hours of exposure or *Daphnia magna* (water flea, a planktonic crustacean) following 48 hours of exposure. In a 96 hour exposure study, 1,000 mg/l WAF slightly inhibited algae (*Pseudokirchneriella subcapitata*) growth, but did not affect biomass.

The concentrations of metals, sulfur and PAHs in the WAF in waters used for the toxicity tests summarized above were all below the quantitation limits (0.4-200 ug/L, 5,100 ug/L, and 5 ug/L, respectively) indicating limited amount of substances were leaching into solution.

Oil Sands Petroleum Coke Leachate Chronic Toxicity[3]

Green coke leachate chronic toxicity to a sensitive planktonic crustacean (*Ceriodaphnia dubia*) was very low. Leachate was prepared by mixing water and coke at a 4:1 ratio under both pH 5.5 (acidic) and pH 9.5 (basic) conditions and allowing the mixtures to age for 15 days. Overlying water, and pore water within the coke solids, were obtained by filtration. The waters obtained (leachate) were only chronically toxic to *Ceriodaphnia dubia* at very high concentrations (6.3% to 31.3% leachate, depending on pH). The chronic toxicity of a low pH (pH = 5.5) leachate could not be determined because the 7d IC50 was less than the lowest concentration tested (6.25%). However, based on other toxicity observations, the toxicity of the pH 5.5 leachate was likely still very low, likely in the low single digit % range.

Toxicity identification procedures indicated the chronic leachate toxicity observed was caused by nickel and vanadium.

Hazard Assessment

The potential exposure of humans to chemicals in petroleum coke in surface waters is minimal, since petroleum coke has a low bioaccumulation potential[1], some or all of the particulate matter entering surface waters would partition to the sediment[2], and the leaching of materials from green coke into water is very limited[2].

Polycyclic aromatic hydrocarbons (PAHs), including a known carcinogen (benzo(a)pyrene), are components of petroleum coke. However, it is expected that very little PAH will partition to water if petroleum coke is released because the solubilities of PAHs are extremely low. For example, PAH concentrations were not quantifiable in water (<5 ug/l) exposed to petroleum coke during the acute aquatic toxicity testing described above[2].

Sulfur is a component of petroleum coke, but is not a toxicological concern in terms of human health from a surface water exposure pathway or aquatic life.

Nickel and vanadium have been identified as a source of toxicity to aquatic life from petroleum coke, but only at very high concentrations of 15-day coke leachate, as described above[3].

We further assessed the hazards of nickel and vanadium to human health and aquatic life by determining the amount of green coke that would need to be discharged to the Detroit River for

the human health and aquatic life protection values to be exceeded[4]. Despite an assumption that all the metals present in petroleum coke as reported in the API hazard characterization report[2] would be available, the calculations indicate that very large quantities of green coke would have to be released to the Detroit River before human health and aquatic life values would be exceeded:

Human health:

Nickel: >347,168 tons green coke (>13,101 dump truck loads)
Vanadium: >1,826 tons green coke (>69 loads)

Aquatic life:

Nickel: >6,944 tons green coke (>262 loads)
Vanadium: >930 tons green coke (>35 loads)

Larger amounts would need to be released to exceed the less restrictive acute water quality criteria.

These calculations are likely conservative, since nickel and vanadium concentrations detected in a sample of the Detroit Bulk Storage pile were less than concentrations reported in the API hazard characterization report.

Like any solid, petroleum coke could interfere with aquatic life by physical effects such as clogged gills or burying of sediment-dwelling organisms if released in very large quantities, and if density was sufficient for the coke to sink.

Conclusions

The primary constituent of green coke, elemental carbon, does not pose a significant risk to human health from a surface water exposure pathway, or to aquatic life. PAH constituents in green coke are unlikely to enter the water column at concentrations of concern because of limited solubility. The primary concern is the potential impacts of heavy metals (dominated by nickel and vanadium) present in green coke. However, a comparison of toxicity-based human health and aquatic life water quality criteria for nickel and vanadium with amounts present in green coke indicates that very large amounts (tons daily) of green coke would need to be released to the Detroit River before surface water quality criteria would be exceeded.

References

[1]EPA 2011. Screening-level characterization. Petroleum coke category. U.S. EPA Hazard Characterization Document. OPPT, Washington, D.C. 20 pp. http://www.epa.gov/chemrtk/hpvis/hazchar/Category_Petroleum%20Coke_June_2011.pdf

[2]API 2007. Petroleum coke category analysis and hazard characterization. American Petroleum Institute. 35 pp. http://www.epa.gov/hpv/pubs/summaries/ptrlcoke/c12563rr2.pdf

[3]Puttaswamy, N. and K. Liber. 2011. Identifying the causes of oil sands coke leachate toxicity to aquatic invertebrates. Environ. Toxicol. Chem. 30(11): 2576-2585.

[4]12.5% of the lowest monthly Detroit River 95% exceedance flow; Michigan DEQ, Lansing, MI

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